



Ultrafast degradation of micropollutants in water *via* electro-periodate activation catalyzed by nanoconfined Fe₂O₃

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ABSTRACT

Herein, we developed and evaluated an electrochemical periodate (PI) activation system for the ultrafast degradation of aqueous micropollutants ($\tau < 3$ s). Filters constructed from carbon nanotubes (CNT) coated with Fe₂O₃ nanoparticles on the outer (Fe₂O₃-out-CNT) and inner surfaces (Fe₂O₃-in-CNT) were prepared to regulate the generation of reactive oxygen species (ROS) during PI activation. The activation function of the electroactive nanohybrid filters lay in their ability to facilitate the redox cycling of Fe(III)/Fe(II) assisted by an electric field. The results showed that a non-radical (i.e., ¹O₂) pathway dominated the degradation process in the electro/Fe₂O₃-in-CNT/PI system, while a contrastive radical pathway (i.e., HO[•] and IO₃[•]) was identified in the electro/Fe₂O₃-out-CNT/PI system. The electro/Fe₂O₃-in-CNT/PI system exhibited enhanced catalytic activity towards the micropollutants degradation relative to its electro/Fe₂O₃-out-CNT/PI counterpart. Density functional theory calculations suggested that PI could be directly decomposed under the nanoconfined environment, rather than forming a stable adsorption complex in the unconfined system.

1. Introduction

Growing concern for micropollutants is gained due to their potential negative effects on aquatic ecosystem and human health [1–3]. However, conventional wastewater treatment technologies such as biological degradation, physical adsorption, and chemical oxidation failed to decontaminate these micropollutants due to limitations associated with sluggish reaction kinetics, poor stability and/or limited selectivity [4–6]. It is, therefore, imperative to seek advanced and innovative strategies to eliminate these micropollutants from water.

Recently, periodate (PI, IO₄[−])-based advanced oxidation processes have attracted widespread interest for wastewater treatment and protection of the aquatic environment from micropollutants [7–9]. Like other oxyanions, such as hydrogen peroxide (H₂O₂), peroxymonosulfate (PMS), and peroxydisulfate (PDS), the reactivity of PI towards organic

molecule is rather limited ($E^0 = 1.6$ V) [10–14]. Therefore, various strategies (e.g., UV irradiation, ultrasound, alkali, hydroxylamine, and transition metals) have been adopted to activate PI into more reactive intermediates (e.g., HO[•], IO₃[•], O₂^{•−}, and ¹O₂) *via* radical and/or non-radical pathways [8,9,15–17]. Among these, considerable efforts have been devoted to the use of transition metal-based heterogeneous catalysts due to their abundance and cost-effectiveness [18–20]. For example, Zong et al. [21] reported that PI can be effectively activated by nano zero-valent iron, leading to enhanced organic degradation performance. However, their relatively low activation efficiency and poor stability remains a challenge due to poor mass transport kinetics in conventional batch reactor as well as potential dissolution of transition metal ions into water [22,23].

To encapsulate those transition metal catalysts into a nanoconfined environment may provide a viable solution to address these

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forementioned limitations. A previous study reported that Fe_2O_3 catalysts confined within carbon nanotubes (CNT) showed a remarkably faster kinetic when compared with a nonconfined counterpart (with Fe_2O_3 loaded onto the outer surface of CNT) toward H_2O_2 activation [24], yet their application is significantly hindered by the challenges associated with their post-separation from the reaction solution. An electrochemical CNT filter functionalized with nanoconfined Fe_2O_3 bring this concept one step further by not only eliminates the necessity of catalyst recovery, but also enables a continuous-flow operation. We previously demonstrated that an electroactive nanohybrid filter, composed of CNT and Fe_2O_3 , could trigger electro-Fenton reactions with tunable radical species [25]. Interestingly, for the system with the Fe_2O_3 coating confined within CNT (i.e., Fe_2O_3 -in-CNT) filter, the dominant reactive species was identified as $^1\text{O}_2$, while that with Fe_2O_3 loaded onto CNT external sidewalls (Fe_2O_3 -out-CNT) was HO^\bullet . One clear advantage of this nanohybrid filter was the adoption of a convection-enhanced mass transport flow-through configuration [26]. Another advantage was the high selectivity of $^1\text{O}_2$ toward electron-rich substances as well as longer lifetime than HO^\bullet (2 μs vs 20 ns) [27]. In addition, the cycling of Fe(III)/Fe(II) couple and system stability could be improved greatly by exerting an external electric field. The working pH could also be extended from acidic to weakly alkaline conditions thanks to the enhanced catalyst stability. Due to the chemical similarities between H_2O_2 and PI, it is reasonable to hypothesize that PI could be also activated by the nanohybrid filter.

The objectives of this study were as follow: 1) develop and evaluate an electrochemical filtration system for efficient PI activation; 2) compare the PI activation performance under confined and unconfined systems from the degradation of representative micropollutants; 3) determine (by experiment/theoretical calculation) the underlying mechanism of the proposed technology and identify the synergistic effects between the electric field, flow-through design, and confined catalysis; 4) examine the practical applicability of the proposed technology. To the best of our knowledge, this is the first attempt to achieve ultrafast degradation of micropollutants using electrochemical PI activation. This study provides a novel design based on an electrochemistry-mediated PI activation system with tunable oxidation pathways in a practical continuous-flow configuration.

2. Materials and methods

2.1. Materials

Potassium periodate (KIO_4 , 99.8%), bisphenol A (BPA, >99.8%), sulfamethoxazole (SMX, 98.0%), 2,4,6-trichlorophenol (2,4,6-TCP, 98.0%), deuterium oxide (D_2O , 99.9%), L-histidine ($\geq 99.0\%$), 2,2,6,6-tetramethylpiperidine (TEMP, $\geq 98.0\%$), 5,5-dimethyl-1-pyrrolidine-N-oxide (DMPO, 97.0%), and methyl phenyl sulfoxide (PMSO, >98.0%) were obtained from Shanghai Aladdin Biological Technology Co., Ltd. (Shanghai, China). Iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\geq 98.0\%$), nitric acid (HNO_3 , 65.0–68.0%), sodium hydroxide (NaOH , $\geq 96.0\%$), potassium phosphate (KH_2PO_4 , $\geq 98.0\%$), sodium chloride (NaCl , $\geq 98.0\%$), sodium sulfate (Na_2SO_4 , $\geq 99.0\%$), sodium nitrate (NaNO_3 , $\geq 98.5\%$), methylene blue (MB), phenol, levofloxacin (LFX), furfuryl alcohol (FFA, $\geq 98.5\%$), *tert*-butyl alcohol (TBA, $\geq 98.0\%$), *p*-benzoquinone (*p*-BQ, $\geq 98.0\%$), tetracycline (TC, $\geq 98.0\%$), and ethanol ($\geq 96.0\%$) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Methanol ($\geq 99.9\%$), phosphoric acid, formic acid and acetonitrile ($\geq 99.9\%$, chromatographic grade) were from Titan Scientific Co., Ltd. (Shanghai, China). Multiwalled CNT (diameter, 10–20 nm, length, 0.5–2.0 μm) were supplied by Nanjing XFNANO Materials Tech Co., Ltd. (Nanjing, China). Ultrapure water (resistivity $\geq 18.2\text{ M}\Omega\text{ cm}$) was used in all experiments.

2.2. Experimental setup and procedures

Fe_2O_3 in/out CNT (denoted as Fe_2O_3 -in-CNT and Fe_2O_3 -out-CNT, respectively) hybrid filters were prepared according previous procedures with minor modifications [24,25,28]. The preparation procedure is given in Text S1.

Electrochemical filtration experiments were performed at $25 \pm 1^\circ\text{C}$ in an electrochemistry-modified Whatman polycarbonate filtration casing (Fig. S1). Two operational modes (i.e., single-pass filtration and batch) were performed for comparison. The hybrid filter was operated cathodically and was electrically connected via a Ti ring and rod to the DH1766A-1 high precision DC power supply (Beijing, China). A perforated Ti sheet was operated as anode. A ISM833C peristaltic pump (Ismatec, Switzerland) was used to control the flow rate. Prior to the degradation experiments, filters were first adsorption saturated by passing a solution of BPA (180 mL of 0.022 mM) through the device for 2 h. For the electrochemical filtration experiments, BPA feed solution (50 mL of 0.022 mM) and PI (2.0 mM) were passed through the flow-through reactor (Fig. S2). For the batch mode, the hybrid filter cathode and Ti sheet anode were put into a glass reactor containing 50 mL of 0.022 mM BPA and 2.0 mM PI solution at -1.5 V . The role of dissolved oxygen was investigated by pre-purging the BPA solution with N_2 before passing through the reactor. Solution pH was adjusted using HCl or NaOH (1.0 mM each). Aqueous samples (1.0 mL) from each experiment were then collected periodically and filtered (0.22 μm polyester membrane filter) prior to analysis (see below). All experiments were conducted in triplicate to ensure reproducibility.

2.3. Analytical methods

The concentrations of BPA, 2,4,6-TCP, TC, LFX, phenol, SMX, FFA, IO_4^- , and IO_3^- were determined by HPLC with variable wavelength detector (VWD) detection following separation on a COSMOSIL 5 C-18-MSII column (Nacalai Tesque, Kyoto, Japan) using an Alliance 2695 Separation Module (Waters, USA). Detailed operational parameters are given in Table S1. BPA degradation intermediates were identified by liquid chromatography-mass spectrometry (LC-MS) using a LC1290 infinity-6470 LC-MS system (Agilent, Singapore). The concentration of MB was measured by a UV-vis spectrometry ($\lambda_{\text{max}} = 665\text{ nm}$) on a UV2600 spectrophotometer (Shimadzu, Japan). The concentrations of leaching Fe ions were measured by inductively coupled plasma mass spectrometry (ICP-MS) using an iCAPTM Q (Thermo Scientific, USA). Reactive species were identified by quenching experiments, using TBA, FFA, *p*-BQ, or PMSO as the scavenging agent, and by electron paramagnetic resonance (EPR) with an EMXnano spectrometer (Bruker, Beijing, China) using DMPO or TEMP as the spin-trapping agent.

2.4. Theoretical calculations

The density functional theory (DFT) calculations were performed by using the Gaussian 09 program [29]. B3LYP was employed with the 6-31G(d) basis set to treat O, C, and H elements. The LANL2DZ basis set was used to treat Fe and I. A (6,6) CNT model with five cell replication units was constructed, in which all boundary C atoms were saturated by H atoms. A Fe-O unit was used to mimic the Fe_2O_3 .

3. Results and discussion

3.1. Characterization of confined and unconfined nanohybrid filters

The Fe_2O_3 -in-CNT and Fe_2O_3 -out-CNT samples were synthesized via a wet chemistry method [24,30]. Due to the presence of oxygen containing groups (e.g., carbonyl groups), CNT are enable to adsorb Fe^{3+} from the acetone/ $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution via electrostatic force [31–33]. Then, Fe_2O_3 nanoparticles could be *in-situ* formed within the channel or on the outer sidewall of CNT afterword the ultrasonic,

stirring and calcination treatment (see Text S1 for the detailed preparation procedure). The morphology of CNT after pre-oxidation treatment was first examined by transmission electron microscopy (TEM). The images showed that the CNT with closed tips and open tips were obtained (Fig. S3). Representative high-angle annular dark-field scanning TEM images suggested that the Fe_2O_3 nanoparticles were randomly distributed within the CNT channels of the Fe_2O_3 -in-CNT (Fig. 1(a)) and on the outer CNT sidewalls of the Fe_2O_3 -out-CNT (Fig. 1(b)). These results demonstrated that the location of the Fe_2O_3 nanoparticles could be regulated by tailoring the CNT pre-oxidation conditions as well as the subsequent wet chemistry parameters during the fabrication process.

Mössbauer spectroscopy was employed to examine the valence state and coordination environment of iron (Text S2). The ^{57}Fe Mössbauer spectra (Fig. 1(c), (d)) and corresponding fitting parameters (Table S2) suggest the sole presence of Fe^{3+} species on both Fe_2O_3 -in-CNT and Fe_2O_3 -out-CNT samples [34]. Moreover, the Mössbauer spectroscopy measurements provide an insight into the coordination environment of Fe in both samples. Two peaks with different electrical quadrupole splitting (QS) values (0.53 mm/s and 0.96 mm/s), corresponding to Fe^{3+} in octahedral and tetrahedral coordination sites were observed in the Fe_2O_3 -in-CNT (Fig. 1(c)). Nevertheless, only Fe^{3+} in an octahedral coordination site exists in the Fe_2O_3 -out-CNT (Fig. 1(d)), which might be due to the curvature of the graphene sheets in CNT, the corresponding coordination of Fe is different between the concave and convex surfaces of CNT [35]. Moreover, the crystal structure and electronic properties of Fe_2O_3 -in/out-CNT filters were further investigated by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The XRD patterns

show that both Fe_2O_3 -out-CNT and Fe_2O_3 -in-CNT exhibit similar diffraction peaks at 35.6° , 43.3° , and 53.7° , corresponding to the (311), (400), and (422) facets of Fe_2O_3 (PDF#39-1346, Fig. S4). High-resolution XPS confirmed the presence of Fe 2p, C 1s, and O 1s in both samples. As observed in Fig. S5, the Fe 2p peak of Fe_2O_3 -in-CNT was much weaker than that of Fe_2O_3 -out-CNT despite their similar Fe contents, probably due to the limited probe depth of the photoelectrons (3–5 nm) for the detection of Fe_2O_3 inside the CNT [24]. The C 1s spectra (Fig. S6(a)) can be deconvoluted into three peaks centered at 291.0 eV, 287.1 eV, and 284.9 eV, associated with $\pi \rightarrow \pi^*$ transition of carbon atoms of graphene structures, C=O bond, and sp^3 C—C bonds of graphitic carbon, respectively. The O 1s spectra (Fig. S6(b)) could be deconvoluted into R-OH (532.0 eV, surface hydroxyl groups), -COOH (533.6 eV, oxygen in esters and anhydrides) in CNT, and a Fe—O peak (530.0 eV, - FeO_x) group. All the results demonstrated that we have successfully fabricated the Fe_2O_3 -out-CNT and Fe_2O_3 -in-CNT hybrid filters.

3.2. Electrochemical periodate activation for micropollutant degradation

BPA was chosen as a model refractory micropollutant to evaluate the efficacy of electrochemical PI activation system. Fig. 2 shows that there was insignificant degradation of BPA with PI alone (1.2%), and no significant improvement was observed for BPA degradation after applying an electric field (E/PI). This excluded the role of the electric field in PI activation. Control experiments using CNT alone led to inappreciable BPA removal as well (1.1%). Furthermore, comparative experiments

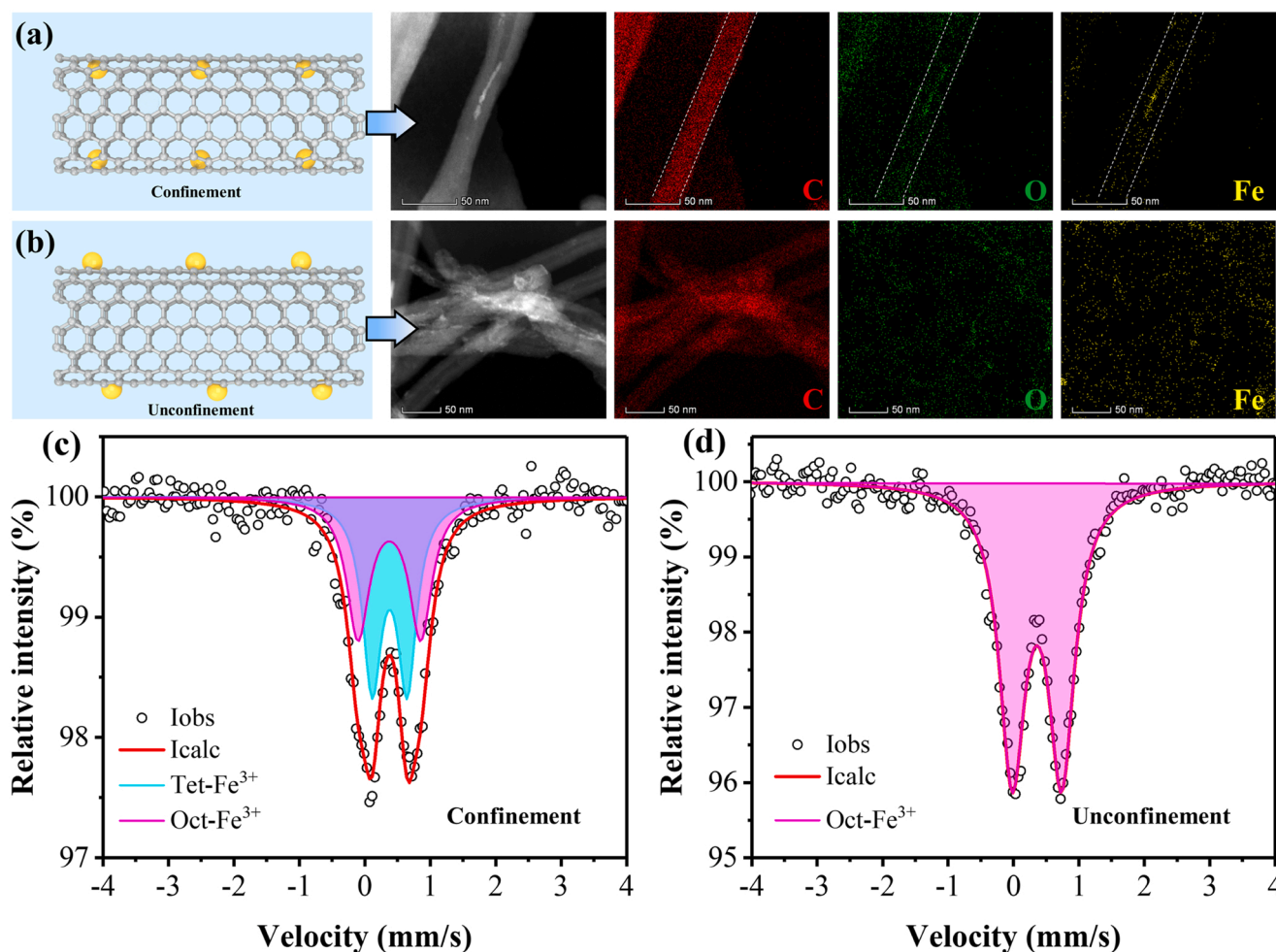


Fig. 1. Illustration of (a) Fe_2O_3 -in-CNT filter and (b) Fe_2O_3 -out-CNT filter, and the corresponding HADDF-STEM and EDX elemental mappings. ^{57}Fe Mössbauer spectra of (c) Fe_2O_3 -in-CNT and (d) Fe_2O_3 -out-CNT recorded at room temperature.

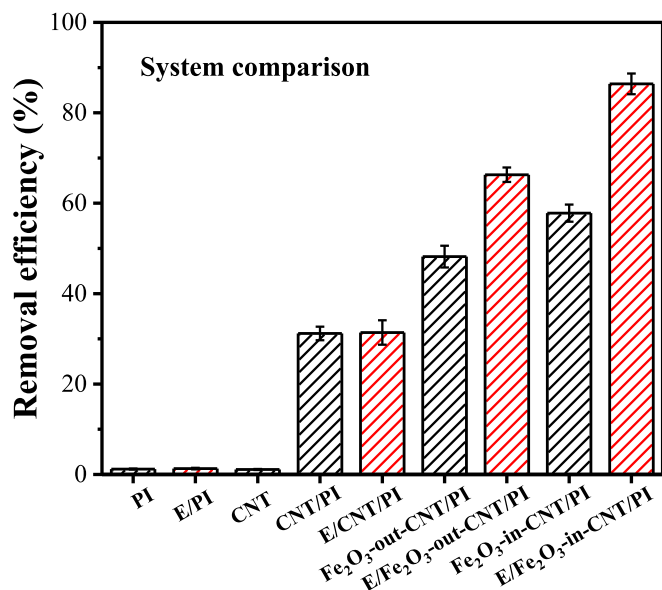


Fig. 2. Degradation of BPA in different systems. Experimental conditions: $[BPA]_0 = 0.022$ mM, voltage = -1.0 V, $[PI]_0 = 1.0$ mM, flow rate = 1.0 mL/min, and $[pH]_0 = 5.7$.

showed that CNT/PI and electro(E)/CNT/PI exhibited similar BPA removal efficiencies (31.2% and 31.4%), thereby the role of the electric field was further excluded. In contrast, the removal efficiency of BPA was appreciably enhanced in the Fe₂O₃-in-CNT/PI and Fe₂O₃-out-CNT/PI systems, which could be attributed to the enhanced cycling of Fe(III)/Fe(II) pairs by the applied electric field. Interestingly, the E/Fe₂O₃-in-CNT/PI system achieved the BPA degradation efficiency as high as 86.4%, a value being approximately 1.3 times of that for E/Fe₂O₃-out-CNT/PI one (66.3%). The significantly enhanced catalytic activity of the E/Fe₂O₃-in-CNT/PI system might be due to a strong electronic interaction between Fe₂O₃ and the CNT interior surface, which accelerates electron transfer from the Fe₂O₃ nanoparticles to the carbon shell [23, 24, 36]. The performance of Fe₂O₃/PI (51.0%) and E/Fe₂O₃/PI (53.2%) is much less than that of E/Fe₂O₃-in-CNT/PI system (86.4%), indicating the indispensable role of CNT (Fig. S7).



Applied voltage played an essential role in the electrochemical treatment process. As indicated in Fig. 3(a), degradation efficiency increased from 64.4% to 91.7% as the applied voltage was declined from -0.5 V to -1.5 V in the E/Fe₂O₃-in-CNT/PI system. No improvement in degradation was observed with further reductions in the applied voltage of -2.0 V, indicating the occurrence of side reactions (Eqs. (1)–(3)). The Fe(OH)₃ generated resulted in the generation of iron sludge which

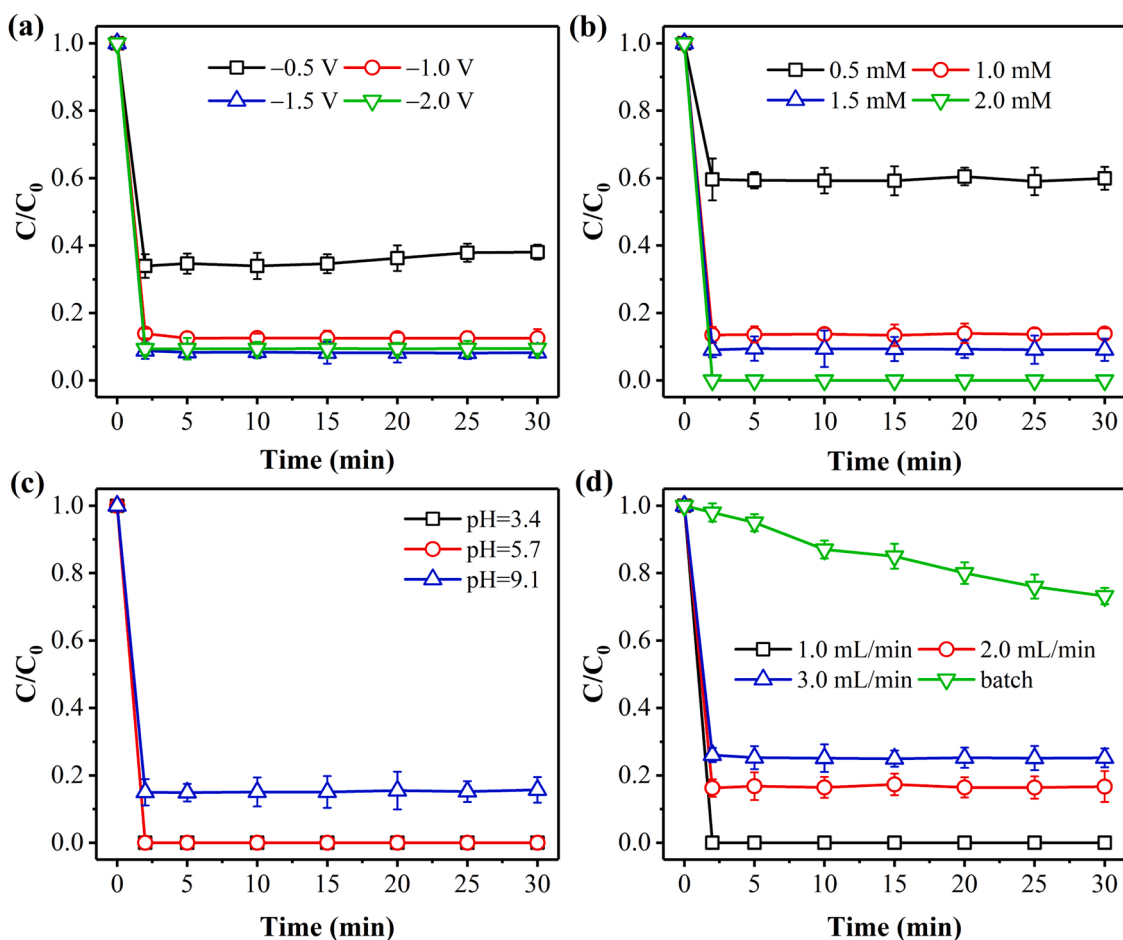


Fig. 3. Effect of (a) applied voltage, (b) PI concentration, (c) solution pH, and (d) flow rate on the degradation of BPA in the E/Fe₂O₃-in-CNT/PI. Experimental conditions: $[BPA]_0 = 0.022$ mM.

decreased the decomposition efficiency of PI. Fig. 3(b) shows the impact of PI concentration on BPA removal in the E/Fe₂O₃-in-CNT/PI system. The removal efficiency of BPA was increased from 40.5% (0.5 mM PI) to 100% (2.0 mM PI), suggesting that the production of ROS increased with increasing PI concentration. Additionally, the solution pH also had a significant impact on the oxidative capability of PI and the removal efficiency of BPA. The removal efficiency of BPA decreased from 100% to 84.8% as the solution pH increased from 3.4 to 9.1 (Fig. 3(c)). The relatively high pH tolerance of the E/Fe₂O₃-in-CNT/PI degradation system (84.8% degradation at pH 9.1) represented a significant improvement in performance compared with traditional homogeneous Fe-based PI-activation systems which showed significant performance reductions at pH > 3.0 [7]. The effects of flow rate on BPA removal efficiency are shown in Fig. 3(d). As the flow rate increased from 1.0 to 3.0 mL/min, BPA removal efficiency decreased from 100% to 74.6%. This was mainly due to the reduced residence time and contact between reactants and active sites at the higher flow rates. Noticeably, when compared with a conventional batch reactor (26.8% in 30 min), the flow-through configuration demonstrated a 3.7-fold increase in BPA degradation efficiency by virtue of the convection-enhanced mass transport.

The efficacy of the E/Fe₂O₃-in-CNT/PI system towards the degradation of other organic pollutants, e.g., LFX, MB, SMX, TC, and 2,4,6-TCP was also evaluated. Fig. S8 shows that under the same conditions of operation, the degradation efficiencies of these additional pollutants were > 85.0% under the single-pass mode. The effect of different oxidants (i.e., H₂O₂, PDS, and PMS) on BPA removal efficiency was also

investigated. Fig. S9(a) reveals that the BPA removal efficiencies follow the decreasing order of E/Fe₂O₃-in-CNT/PI (100%) > E/Fe₂O₃-in-CNT/PMS (96.3%) > E/Fe₂O₃-in-CNT/PDS (56.7%) > E/Fe₂O₃-in-CNT/H₂O₂ (39.3%). Although the E/Fe₂O₃-in-CNT/PMS system also exhibited excellent initial high degradation performance (>90%), its long-term efficiency decreased by 46.5% after 48 h continuous operation, thus limiting its practical application (Fig. S9(b)). Hence, the E/Fe₂O₃-in-CNT/PI system might be a promising and effective alternative advanced oxidation process for wastewater remediation.

3.3. Mechanistic insights

The essential ROS responsible for organic degradation in the E/Fe₂O₃-in-CNT/PI and E/Fe₂O₃-out-CNT/PI systems were identified using quenching experiments and EPR analysis. TBA was used as the scavenger for HO• ($k = (3.8\text{--}7.6) \times 10^8 \text{ mol}^{-1} \text{ s}^{-1}$) [8]. FFA and PMSO were the scavengers for ¹O₂ ($k = 1.2 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1}$) [37] and high-valence Fe-oxo species, respectively. In addition, *p*-BQ was employed as scavenger for O₂•⁻ ($k = (0.90\text{--}1.00) \times 10^9 \text{ mol}^{-1} \text{ s}^{-1}$) [38]. As shown in Fig. 4(a), the addition of TBA and PMSO showed limited inhibition on BPA degradation in the E/Fe₂O₃-in-CNT/PI system. In contrast, the addition of FFA (100 mM) almost completely inhibited the BPA degradation (to 3.5%), indicating ¹O₂ was the dominant ROS. Furthermore, the presence of *L*-histidine (another ¹O₂ scavenger [39]) similarly hindered the BPA removal performance (Fig. S10). Considering FFA or *L*-histidine could be directly consumed by PI, control experiments between PI (2.0 mM) and FFA (100 mM) or *L*-histidine (100 mM) were

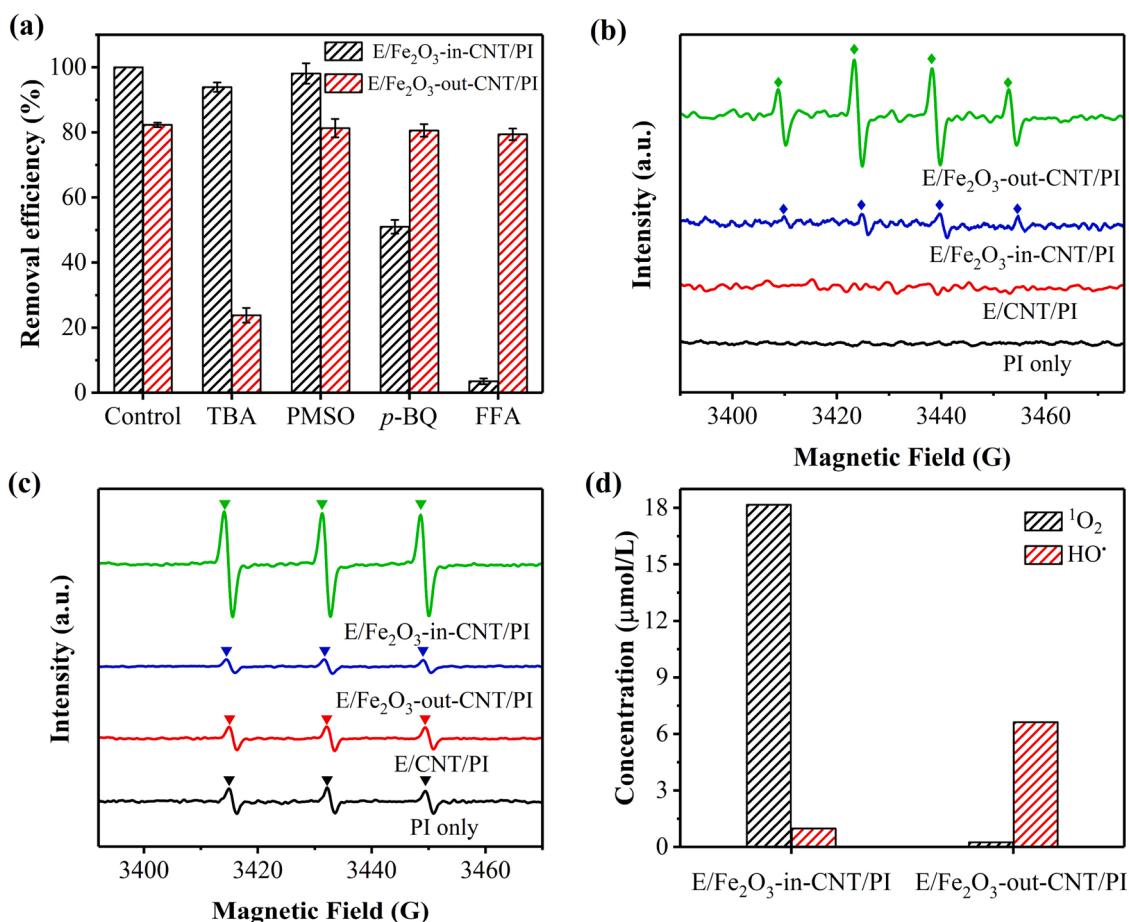
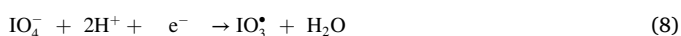
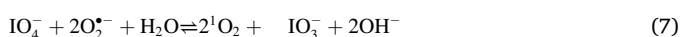
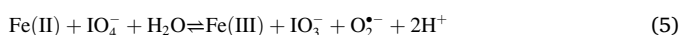


Fig. 4. Identification of reactive oxidizing species: (a) quenching tests with different radical scavengers. (b) EPR characterization using DMPO in the absence of BPA. (c) EPR characterization using TEMP in the absence of BPA. (d) quantitative determination of ¹O₂ and HO•, respectively. Experimental conditions: [TBA]₀ = 100 mM, [FFA]₀ = 100 mM or 1.0 mM, [*p*-BQ]₀ = 50 mM, [PMSO]₀ = 5.0 mM, [DMPO]₀ = [TEMP]₀ = 50 mM, [BPA]₀ = 0.022 mM, [PI]₀ = 2.0 mM, [pH]₀ = 5.7, voltage = −1.5 V, and flow rate = 1.0 mL/min.

further performed. As shown in Fig. S11 and S12, the interaction between FFA (or L-histidine) and PI was rather negligible, indicating the inability of PI to be oxidized by FFA or L-histidine [8,15,40]. Thus, the inhibition of BPA degradation kinetics was mainly originated from the scavenge of $^1\text{O}_2$ [41]. Thereby, it fully proved that $^1\text{O}_2$ was the main ROS in the E/Fe₂O₃-in-CNT/PI system. The addition of *p*-BQ partially suppressed BPA degradation to 51.0%, indicating the possible contribution of $\text{O}_2^{\bullet-}$ to BPA degradation (Eqs. (4) and (5)). However, the negligible degradation of BPA by $\text{O}_2^{\bullet-}$ was probably due to its mild oxidative capability (Fig. S13), indicating that it might be a key intermediate in $^1\text{O}_2$ generation during PI activation. The *in situ* generated $\text{O}_2^{\bullet-}$ could then recombine to form $^1\text{O}_2$ (Eq. (6)). Besides, the direct oxidation of $\text{O}_2^{\bullet-}$ to $^1\text{O}_2$ by residual PI is also a thermodynamically possible alternate pathway (Eq. (7)).



In the E/Fe₂O₃-out-CNT/PI system, the introduction of TBA inhibited the degradation of BPA by 58.5%, highlighting the significant contribution from HO^\bullet toward the BPA degradation. While the presence of FFA (1.0 mM), PMSO (5.0 mM) and *p*-BQ (50 mM) demonstrated negligible inhibition on the BPA elimination, further ruling out the involvement of $^1\text{O}_2$, high-valence Fe-oxo species, and $\text{O}_2^{\bullet-}$ to the BPA degradation process. It should be noted that FFA, *p*-BQ or PMSO could also be oxidized by HO^\bullet due to its non-selectivity. However, the addition of FFA (or *p*-BQ, PMSO) in the E/Fe₂O₃-out-CNT/PI system showed limited suppression on the BPA degradation kinetics. It has been previously reported that low concentration of FFA (<10 mM) may not react with HO^\bullet due to mass transport limitations [42]. Although *p*-BQ could react with HO^\bullet to suppress the BPA degradation, it also assumed a role as electron shuttle to accelerate the Fe(III)/Fe(II) cycle and to promote BPA degradation simultaneously [43]. These two concurrent processes may not significantly change the overall BPA degradation kinetics. While the interaction between HO^\bullet and PMSO may lead to the generation of $[\text{Fe}^{\text{IV}}\text{O}]^{2+}$ and/or $\equiv\text{Fe}^{\text{III}}(\text{O}_2\text{H})$, which might be responsible for the subsequent degradation of BPA [44]. Furthermore, a BPA degradation of 23.8% could still be observed in the presence of excessive TBA (100 mM), possibly resulting from the generation of IO_3^\bullet in the E/Fe₂O₃-out-CNT/PI system.

Although a conclusive method for the detection of IO_3^\bullet is still unavailable, the possible generation of IO_3^\bullet could be indirectly verified via scavenging experiments and the degradation of selected pollutants [16, 21,45]. For example, it has been reported that the IO_3^\bullet was unreactive towards 2,4,6-TCP [45]. Under test, 2,4,6-TCP was effectively degraded (97.8%) in the E/Fe₂O₃-in-CNT/PI system suggesting that a contribution from IO_3^\bullet could be ignored (Fig. S8). The contribution of IO_3^\bullet to degradation of pollutants in the E/Fe₂O₃-out-CNT/PI system was also investigated using phenol, SMX, and 2,4,6-TCP. The results given in Fig. S14 show that phenol (97.4%) and SMX (87.6%) were efficiently degraded in the E/Fe₂O₃-out-CNT/PI system [45,46], while 2,4,6-TCP was partially removed (35.8%) under the same conditions. These results indicated that IO_3^\bullet might be involved in the degradation of organic compounds in the E/Fe₂O₃-out-CNT/PI system, which can be formed by reduction of IO_4^- at the surface of the Fe₂O₃-out-CNT cathode (Eq. (8)).

EPR-spin trapping was also used to directly verify essential ROS. No characteristic peaks were observed in the EPR spectra obtained from PI or CNT in the presence of DMPO (Fig. 4(b)). As expected, the characteristic quadruple peak signals of DMPO- HO^\bullet (1:2:2:1) were observed in the E/Fe₂O₃-out-CNT/PI system. The intensity of the corresponding

signal from the E/Fe₂O₃-in-CNT/PI system was much weaker than that of E/Fe₂O₃-out-CNT/PI system, which agreed with the radical quenching tests. Noticeably, a 1:1:1 triplet signal of TEMP- $^1\text{O}_2$ was observed in all four systems in the absence of BPA, indicating the presence of $^1\text{O}_2$ (Fig. 4(c)). Compared with other systems, the intensity signal of $^1\text{O}_2$ was much greater in the E/Fe₂O₃-in-CNT/PI system. Besides, the lifetime of $^1\text{O}_2$ in D₂O (22–70 μs) was 10-fold longer than that in H₂O (2 μs) [47]. Thereby, the EPR measurements of $^1\text{O}_2$ were performed by replacing the ultrapure water as D₂O. As observed in Fig. S15, the signal intensity of $^1\text{O}_2$ was markedly increased when using D₂O as the solvent, which provide another solid evidence on the $^1\text{O}_2$ generation. The addition of FFA would significantly suppress the signal intensity of $^1\text{O}_2$ (Fig. S16). Furthermore, the EPR spectra in the presence of 10 mM *p*-BQ (quenching agent of $\text{O}_2^{\bullet-}$) leads to evidently weakened $^1\text{O}_2$ signal intensity (Fig. S16), indicating $\text{O}_2^{\bullet-}$ may be the key intermediate for the $^1\text{O}_2$ generation. Here, $^1\text{O}_2$ may arise from the recombination of $\text{O}_2^{\bullet-}$, generated as an intermediate from PI and oxygen [48]. To verify this hypothesis, a control experiment was conducted in deoxygenated condition obtained by pre-purging the BPA solution with N₂. The results in Fig. S17 showed that BPA degradation efficiency was not affected by N₂ atmosphere, implying that the contribution of dissolved oxygen to BPA degradation was negligible. In addition, the EPR signal from TEMP- $^1\text{O}_2$ adduct in the E/Fe₂O₃-in-CNT/PI system was not suppressed under the N₂ purged environment (Fig. S18). This suggested that $^1\text{O}_2$ was not derived from the dissolved oxygen.

A previous study demonstrated that the CNT-mediated electron transfer process played a dominant role toward the elimination of organic contaminants in CNT/PI system [49]. For the purpose of analyzing the electron transfer processes, linear sweep voltammetry (LSV) was performed to monitor the current response in both E/Fe₂O₃-out-CNT/PI and E/Fe₂O₃-in-CNT/PI systems. As shown in Fig. S19, both Fe₂O₃-out-CNT and Fe₂O₃-in-CNT filters showed no evident current increase in the existence of PI and BPA. This ruled out the possibility of an electron transfer process between BPA (electron donor) and PI (electron acceptor) in both systems.

To further compare the key ROS produced in confined and unconfined system, the concentrations of $^1\text{O}_2$ and HO^\bullet were determined by using EPR method on a quantitative basis. As shown in Fig. 4(d), the HO^\bullet concentration of 6.6 μmol/L obtained for E/Fe₂O₃-out-CNT/PI system was 6.8 times higher than that of 0.98 μmol/L for E/Fe₂O₃-in-CNT/PI system. In comparison, $^1\text{O}_2$ concentration (0.24 μmol/L) was more than one order of magnitude lower than that of E/Fe₂O₃-in-CNT/PI system (18.2 μmol/L). These results confirmed the dominance of different ROS in the E/Fe₂O₃-in-CNT/PI and E/Fe₂O₃-out-CNT/PI systems, possibly due to the contrasting interactions of Fe₂O₃ with the interior/exterior CNT walls.

Based on these investigations, different working mechanisms were proposed for the unconfined and confined Fe₂O₃ filter systems (Fig. 5). The results indicated that BPA degradation in the E/Fe₂O₃-out-CNT/PI system was a dual radical (HO^\bullet and IO_3^\bullet) process, in which HO^\bullet accounted for the majority of the degradation process (58.5%). The following mechanism of PI activation was proposed: Fe(III) on the surface of E/Fe₂O₃-out-CNT filter cathode is reduced to Fe(II) (Eq. (4)); the interaction between Fe(II) and PI leads to HO^\bullet generation, similar with the Fenton reaction. This appeared to be quite similar as the single-electron-transfer reactions of IO_4^- photosensitization or zero-valence metals (e.g., Fe⁰-Cu and Fe⁰-Ni systems) [45,50,51], IO_3^\bullet is formed from the reduction of IO_4^- at the E/Fe₂O₃-out-CNT filter cathode (Eq. (8)).

In the E/Fe₂O₃-in-CNT/PI system, $^1\text{O}_2$ was considered as the dominant ROS for BPA degradation and the following mechanism was proposed: i) Fe(III) was rapidly reduced to Fe(II) in the presence of an electric field (Eq. (4)), which then participates in the activation of PI to produce $\text{O}_2^{\bullet-}$ (Eq. (5)). It is speculated that the nanoconfinement changes the PI activation pathways both kinetically and thermodynamically [52]. When compared with nonconfined Fe₂O₃ nanoparticles,

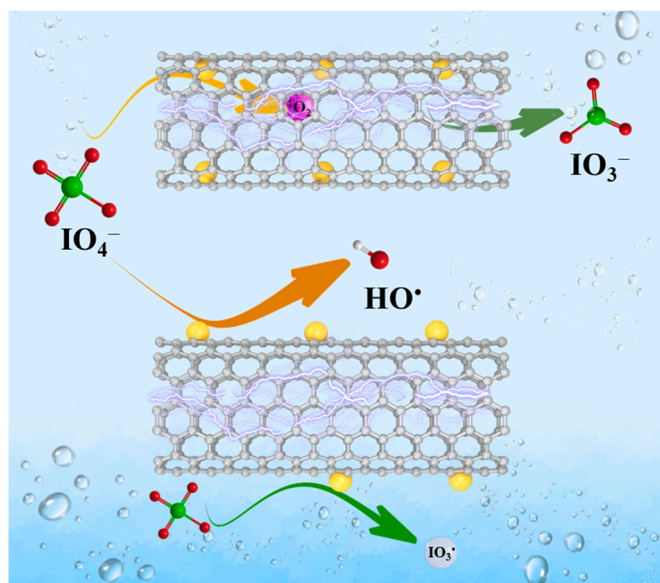


Fig. 5. A schematic illustration of possible mechanism of pollutants degradation in E/Fe₂O₃-in-CNT/PI and E/Fe₂O₃-out-CNT/PI systems.

such nanoconfinement by CNT poses a strong electronic interaction between the electron-deficient CNT concave surface and those encapsulated Fe₂O₃ particles [24,28]. ii) ¹O₂ was produced via the recombination of O₂^{•−} (Eq. (6)) or the reaction of IO₄[−] with O₂^{•−} (Eq. (7)). To gain further insights into the mechanism of PI conversion, the decomposition of IO₄[−] was followed after activation in the E/Fe₂O₃-in-CNT/PI system in the presence and absence of BPA (Fig. S20). In the absence of BPA, only a small fraction of PI (17.5%) was decomposed by the E/Fe₂O₃-in-CNT filter. In contrast, such fraction increased significantly to 77.2% in the presence of BPA. This phenomenon could be explained from the perspective of chemical reaction equilibrium. The presence of BPA consistently consumed the as-produced ¹O₂, leading to the proceed in the forward direction of Eqs. (5)–(7) as well as an enhanced IO₄[−] decomposition efficiency compared with that in the absence of BPA. The reduction of IO₄[−] was accompanied by the stoichiometric formation of IO₃[−], and the overall concentration of iodine remained in balance. Additionally, replacing IO₄[−] by IO₃[−] led to no removal of BPA (Fig. S21). Note that IO₃[−] was the major product of IO₄[−] reduction, as no iodine species, or reduction to I[−], occurred in the system. Specifically, the possible generation of I₂/I₃[−] and HOI could be excluded based on the results obtained using starch chromatometry and phenol as a capturing reagent [53,54], respectively (Text S3, Figs. S22 and S23).

3.4. Theoretical calculations

DFT calculations were conducted to gain a deeper insight into the confinement effect on PI activation. The results showed that the formation of Fe₂O₃-CNT complexes in both Fe₂O₃-out-CNT and Fe₂O₃-in-CNT filters were thermodynamically stable. Fig. 6 shows that PI could be adsorbed onto the surface of Fe₂O₃-out-CNT at distances between the Fe atom and each of the two O atoms of PI of 2.10 and 2.09 angstrom, respectively. In comparison, PI could be directly decomposed in the Fe₂O₃-in-CNT, instead of the formation of a stable adsorption complex. In viewpoint of thermodynamics, the direct decomposition of PI in the Fe₂O₃-in-CNT was 54.3 kcal/mol more favorable than adsorption on the surface of Fe₂O₃-out-CNT. Hence, the DFT calculations suggested that the confinement effect of the Fe₂O₃-in-CNT was important in PI activation, which supported the experimental observations.

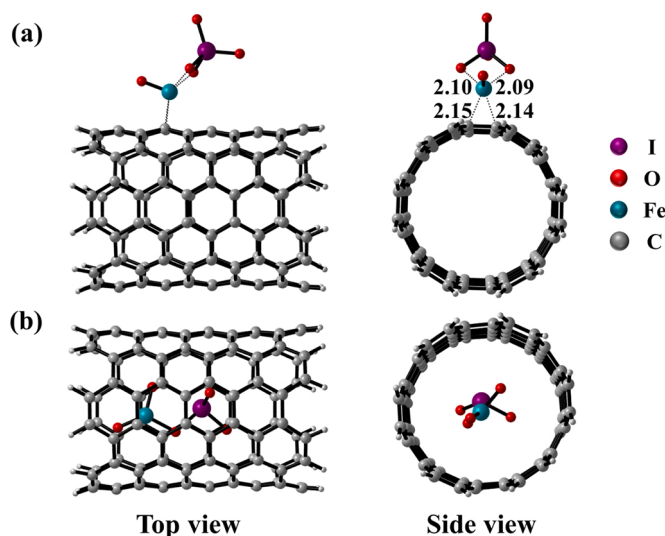


Fig. 6. DFT-optimized geometries of (a) Fe₂O₃-out-CNT and (b) Fe₂O₃-in-CNT with PI.

3.5. BPA degradation pathways

Identification of the BPA degradation intermediates was an important step in understanding the mineralization mechanism. Fig. S24 shows the key intermediates detected by LC-MS in the E/Fe₂O₃-in-CNT/PI degradation system of BPA. Seven degradation intermediates were identified with *m/z* values of 244, 260, 266, 238, 192, 176, and 214 amu.

The Fukui index based on natural population charge (Text S4) was used to predict the active sites of BPA (Fig. S25(a) and (b)). As the main active species, ¹O₂ was classified as an attacking nucleophile, i.e., it favored sites that could readily lose an electron. Hence, the Fukui index (*f*⁺) was used to determine the potential electrophilic sites of BPA and the distribution of *f*⁺ is illustrated in Fig. S25(c). C15 (*f*⁺ = 0.0656) and C25 (*f*⁺ = 0.0652) gave the highest Fukui indices, indicating the most active sites on BPA. Based on these values and the molecular weights of the detected intermediates, degradation pathways for BPA (228 amu) were proposed (Fig. 7). In pathway I, oxidation of the benzene ring from the nucleophilic addition of ¹O₂ at the C15 and C25 active sites leads to the formation of products A (244 amu; single oxygen atom) and B (260 amu; two oxygen atoms). Following ring-opening, product C (266 amu) is formed, from which products D (238 amu) and E (192 amu) are formed C (266 amu) by oxidation. Cleavage of the C–C bond of product E (192 amu) led to the formation of F (176 amu). In pathway II, product G (214 amu) was obtained from the demethylation of BPA (228 amu). Finally, all the above intermediates could be degraded into smaller molecules (e.g., carboxylic acids) and further mineralized to CO₂ and H₂O.

3.6. Evaluation of practical applications

3.6.1. Effect of water chemistry

Due to the high specificity of ¹O₂ towards BPA, it was inferred that the E/Fe₂O₃-in-CNT/PI system might exhibit high selectivity towards the pollutant in complex aqueous matrices. Hence, the impacts of inorganic constituents and natural organic matters (e.g., humic acid, HA) on the degradation of BPA were investigated. As expected, the presence of these materials had a negligible influence on the degradation of BPA (Fig. S26(a)). The efficacy of the E/Fe₂O₃-in-CNT/PI system was also evaluated using tap water and the lake water (Fig. S26(b)). The results showed that BPA degradation efficiencies of 94.3% and 81.8% could be achieved in spiked tap water and lake water respectively. This indicated effectiveness and reliability of the E/Fe₂O₃-in-CNT/PI system for practical applications.

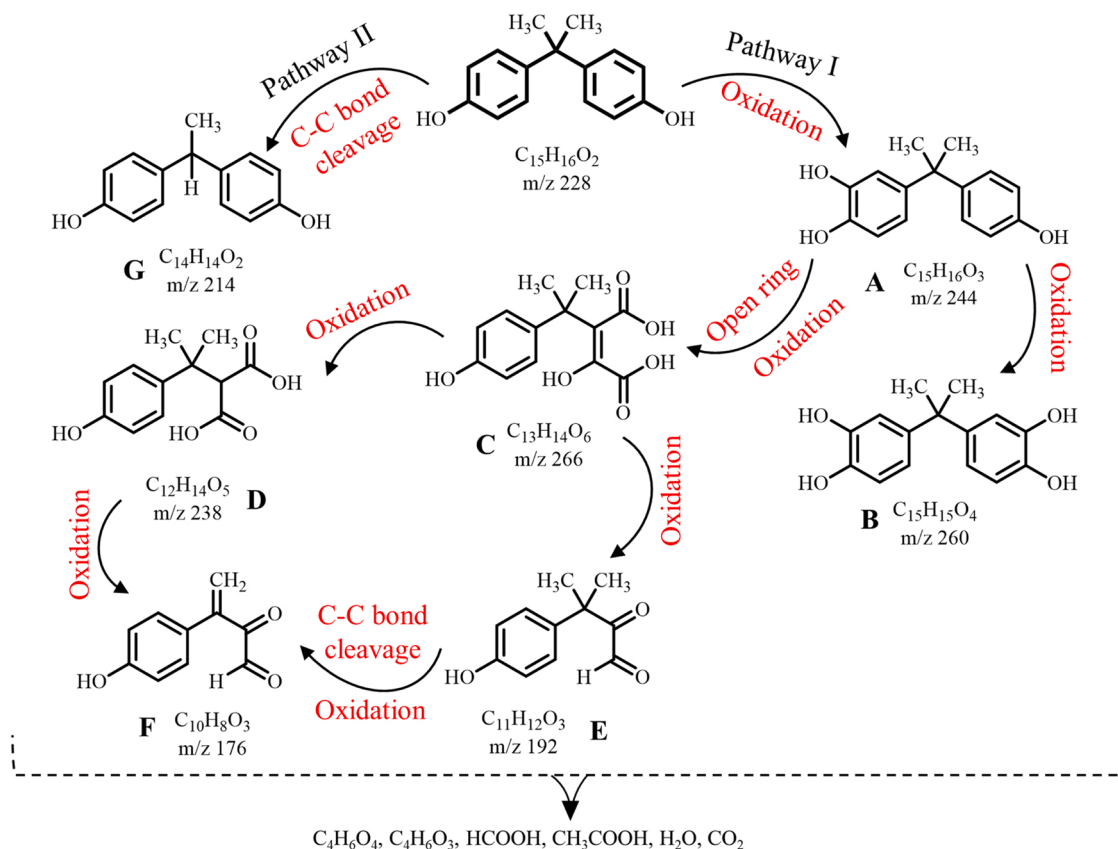


Fig. 7. Possible degradation pathways of BPA in the E/Fe₂O₃-in-CNT/PI system.

3.6.2. Stability evaluation

Long-term continuous operation (48 h) in the single-pass mode showed a small reduction (8.9%) in BPA removal efficiency for the Fe₂O₃-in-CNT functional filter (Fig. 8(a)), while that of E/Fe₂O₃-out-CNT/PI was much greater (35.5% after 48 h operation). The difference in performance was attributed to the reduced loss of Fe in the E/Fe₂O₃-in-CNT/PI system (< 10 µg/L) compared with the E/Fe₂O₃-out-CNT/PI system (316.5 µg/L) during operation (Fig. 8(b)). The differences in Fe loss could be due to confinement of Fe₂O₃ within the interior cavity of CNT of the E/Fe₂O₃-in-CNT/PI system, which minimizes corrosion and

leaching.

3.6.3. Energy consumption

Practical wastewater treatments usually require efficient energy utilization [55–57]. Notably, the energy consumption (0.05 kWh/m³) of the E/Fe₂O₃-in-CNT/PI system under optimized conditions (*i.e.*, applied voltage, −1.5 V; electric current, 2.0 mA; flow rate, 1.0 mL/min) (Text S5) was much lower than other electrochemical processes reported in literatures [58–61]. Such low energy consumption could also be associated with the convection-enhanced mass transport, improved catalyst

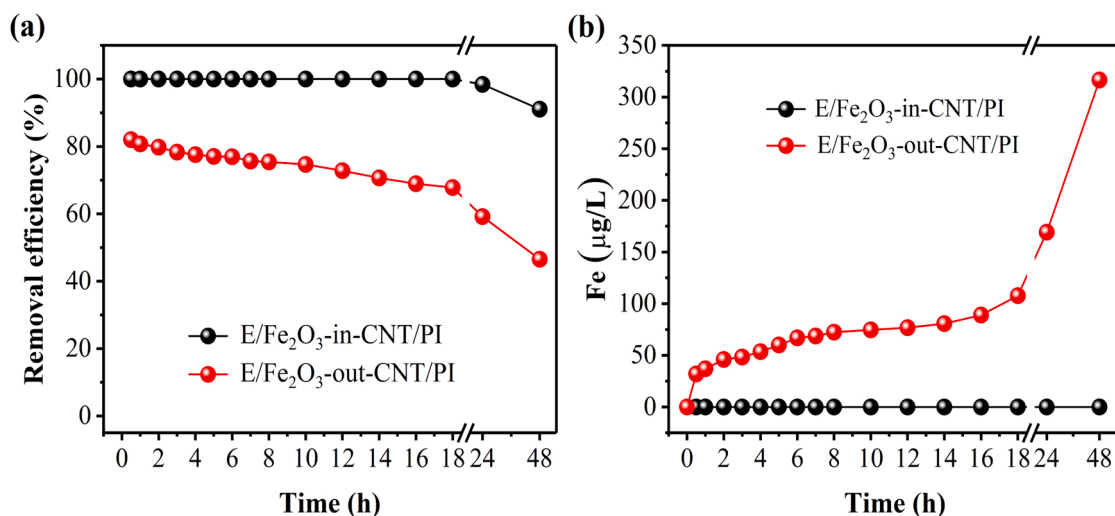


Fig. 8. Evaluation of (a) the long-term stability and (b) Fe leaching of the E/Fe₂O₃-in-CNT/PI and E/Fe₂O₃-out-CNT/PI systems, respectively. Experimental conditions: [BPA]₀ = 0.022 mM, [PI]₀ = 2.0 mM, [pH]₀ = 5.7, voltage = −1.5 V, and flow rate = 1.0 mL/min.

stability, abundant catalytic active sites [62,63] as well as the synergistic effects between electric field and nanoconfined effect.

4. Conclusions

A novel electrochemical PI activation system was developed for the ultrafast and robust degradation of micropollutants. Compared with the radical-dominated pathway observed for the E/Fe₂O₃-out-CNT/PI system, a nonradical-process dominated the E/Fe₂O₃-in-CNT/PI system. The E/Fe₂O₃-in-CNT/PI system demonstrated superior performance over the E/Fe₂O₃-out-CNT/PI system for the degradation of BPA over a wide pH range. BPA removal efficiency of > 90% could be sustained over 48 h operation, suggesting that the Fe₂O₃-in-CNT filter had good stability and reactivity. The results from this study provide further insight into the mechanisms of heterogeneous electrochemistry-mediated PI activation. They may also provide a platform to develop efficient, sustainable, and economical technologies for future water remediation applications.

CRediT authorship contribution statement

Dongli Guo: Data curation, Methodology, Investigation, Writing – original draft. **Yuan Yao:** Formal analysis, Software, DFT calculation. **Shijie You:** Writing – review & editing, Project administration, Resources. **Limin Jin:** Methodology, Validation. **Ping Lu:** Characterization. **Yanbiao Liu:** Conceptualization, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2022.121289.

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